# Origin of Line Broadening in the Hydridic Nuclear Magnetic Resonance of Isothiocyanato-platinum(II) Complexes

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*Summary* The recent suggestion that line broadening in the hydridic n.m.r. resonances of the complexes *trans*-[PtH(*N*CS)$L_2$] is not due to interaction with the $^{14}N$ nucleus is refuted.

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The hydridic regions of the n.m.r. spectra of solutions of *trans*-[PtH(NCS)$L_2$] (L = $Et_3As$, phosphines) comprise two sets of resonances and at ambient temperatures the higher field set usually displays significant broadening. Powell and Shaw[1] attributed this broadening and that observed in analogous cyanato-complexes to interaction between the hydridic proton and the quadrupolar $^{14}N$ nucleus and thence attributed the broadened lines to forms of the complexes that contain Pt–N linkages. On the basis of studies of the effects of temperature and added phosphines on the spectra, Adlard and Socrates have stated that this method of assignment to specific isomers is not acceptable, claiming that ligand exchange appears to be almost solely responsible for the broadening of the resonances in complexes of various phosphines and $Et_3As$.[2,3]

However, results (i)—(iii) suggest that dissociation of L is unlikely to cause significant perturbation of the hydridic resonances.

(i) Dissociation of phosphine ligands from platinum(II) complexes has not been observed in extensive studies of $^1H$- and $^{31}P$-n.m.r. spectra,[4] and there are no anomalies reported for the $^{31}P$ spectrum of *trans*-[PtH(*N*CS)$(Et_3P)_2$].[5] Also, there is no reason to expect the *N*CS or *N*CO groups to labilize the phosphine ligands as their steric requirements are low[6] and their electronic effects are normal for *N*-donors.[7,8]

(ii) The $^{31}P$-spectra of the phosphonato-ligands of *trans* [PtX{$(PhO)_2(O)P$}$(Bu_3P)_2$] are normally sharp triplets [$^2J(PPtP') = 20$—$30$ Hz, X = Cl, Br, I, $ONO_2$, $N_3$, $NO_2$], but broad lines are observed for *X* = *N*CS, *N*CO.[8] Since coupling due to $^2J(PPtP')$ is observed in the resonances of the phosphines (X = *N*CO, *N*CS), the broadening cannot

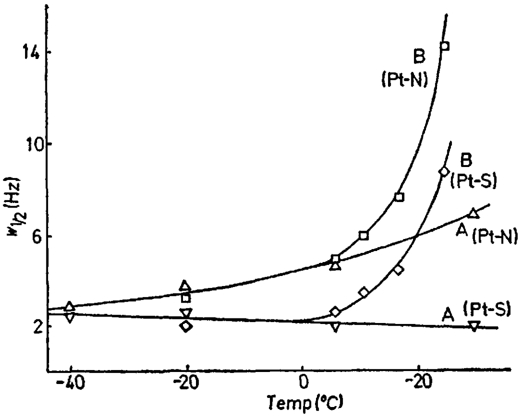

Figure. *Graphs of widths at half height* ($\omega_{\frac{1}{2}}$) *of hydridic resonances against temperature for* $^1H$ (60 MHz) *spectra of* (A) *trans*-[PtH(NCS)$(Et_3P)_2$] (1·2 M) *in* $CDCl_3$, *and* (B) *trans*-[PtH(NCS)$(Et_3P)_2$] (1·2 M) *and* $Et_3P$ (0·22 M) *in* $CDCl_3$. *For each sample the low-field* (Pt–S) *and high-field* (Pt–N) *resonances were recorded on a single scan of the spectrometer, and values of* $\omega_{\frac{1}{2}}$ *for all except the broadest lines were reproducible to within* 0·2 Hz *in the triplet components. The field homogeneity of the spectrometer was slightly better for sample* B.

be due to phosphine exchange, and interaction between the *trans* related $^{31}P$ and $^{14}N$ nuclei is clearly implied.

(iii) Since the hydridic resonances in *trans*-[PtHXL$_2$] (L = phosphine) are triplets through coupling to two $^{31}P$-nuclei, phosphine exchange is expected to broaden the lines of the multiplet. However, broad lines are also reported[1,2] for *trans*-[PtHX(Et$_3$As)$_2$] (X = *N*CS, *N*CO) where the highly quadrupolar $^{75}As$-nuclei have no spin–spin interaction with the hydridic proton. Exchange of Et$_3$As is not therefore expected to broaden the hydridic resonances so the broadening must be attributed to interaction with $^{14}N$.

The dependence of the widths of the hydridic resonances of solutions of *trans*-[PtH(NCS)(Et$_3$P)$_2$] on temperature with and without added Et$_3$P is illustrated in the Figure. At the concentrations employed in sample (B), broadening by added phosphine is negligible below *ca.* −5°, but the high field resonances (labelled Pt–N) are very significantly wider at and below this temperature. There is thus no connection between the broadening of the high field resonance in the absence of phosphine and that caused by addition of phosphine. All the results are consistent with the interpretation of Powell and Shaw,[1] and there is no evidence for phosphine or arsine dissociation having significant effect on the line-widths. Exchange rates on addition of phosphine are fairly similar for the *N*- and *S*-bonded isomers.

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[1] J. Powell and B. L. Shaw, *J. Chem. Soc.*, **1965**, 3879.

[2] M. W. Adlard and G. Socrates, *J.C.S. Chem. Comm.*, 1972, 17.

[3] M. W. Adlard and G. Socrates, *J.C.S. Dalton*, 1972, 797; *J. Inorg. Nuclear Chem.*, 1972, **34**, 2339.

[4] For example see: A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826; A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *ibid.*, 1971, 3833; J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[5] G. Socrates, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1667.

[6] D. W. Meek, P. E. Nipcon, and V. I. Meek, *J. Amer. Chem. Soc.*, 1970, **92**, 5351.

[7] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[8] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.